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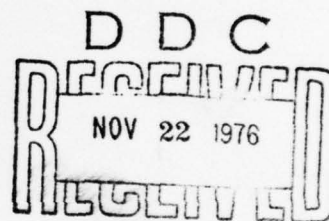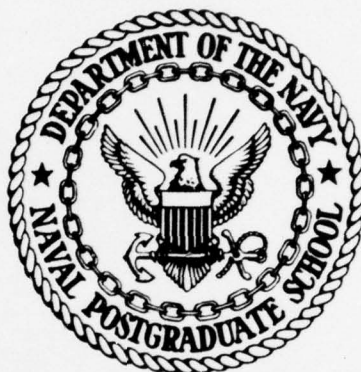# NAVAL POSTGRADUATE SCHOOL
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A REVIEW OF MATERIALS AND MECHANISMS WHICH AFFECT
THE PERFORMANCE OF LEAD-ACID STORAGE BATTERIES

by

Jeff Perkins
J. L. Pokorny
M. T. Coyle

October 1976

NAVAL POSTGRADUATE SCHOOL
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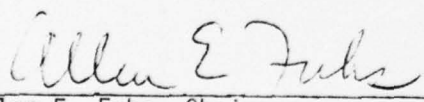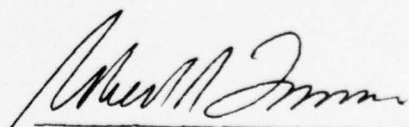Approved for public release;
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TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

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PERFORMANCE OF LEAD-ACID STORAGE BATTERIES

by Jeff Perkins[*]

ABSTRACT

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I. INTRODUCTION

The purpose of this article is to review, from the viewpoint of the materials scientist, the basic principles which govern the properties of the various component materials of lead-acid storage batteries. Although this battery system has been in existence for more than one hundred years, it is still the subject of considerable research and development, an indication of the importance and complexity of the system. From an engineering standpoint, the lead-acid battery is a classical example of the complementary application of diverse materials in a given system. This review will give some attention to the historical aspects of lead-acid battery materials development, but recent developments and contemporary and future materials will be emphasized. Since this paper is intended for a general audience of materials engineers, rather than strictly for battery technologists, the basic features of this battery system, including electrochemical principles and storage battery terminology, will be briefly reviewed prior to discussing the various functional materials in detail.

I.1 Historical perspective

The first lead-acid cell, constructed by Gaston Planté in 1859, consisted of two lead sheets, separated by strips of flannel, rolled together and immersed in dilute sulfuric acid. Planté[1] found that by passing an electric current through the cell for a time (i.e., by "charging" the battery) he could convert the surface of one lead sheet to lead dioxide, and the surface of the other to a spongy lead mass; these processes constitute what is now referred to as "forming" of battery plates. The charged cell then produced a spontaneous current when connected to an external circuit, with the lead dioxide electrode being the positive terminal and the sponge lead electrode the negative terminal. Planté's charged cell exhibited all the basic features typically found in a rechargeable or "secondary" storage battery: (1) structural bases for the two electrodes (in this case the lead sheet, now more typically consisting of and referred to as "grids"); (2) active materials in different energy states at the respective electrodes (the lead dioxide and spongy lead), which will spontaneously react such as to reach an equilibrium condition at discharge, producing energy and electrical current in the process; (3) separators (the flannel) to electrically insulate the electrodes, yet allow electrolyte to permeate; (4) an electrolyte (the dilute H_2SO_4 solution); (5) repeatability of the charge-discharge cycle.

By alternately charging and discharging, Planté found that the storage "capacity" of the cell, which is the total current-time product produced during discharge, was able to be increased; this was because Planté was carrying out what would now be considered "forming" (creation of active materials) and "conditioning" of a storage battery. Because this required a long time with Planté's original crude design, an innovation

1

was soon developed, by Faure[2], in which the positive and negative electrodes were "pasted" with coatings of lead oxides prior to charge-discharge cycling, which reduced the time required to "form" the positive and negative active materials, i.e., to convert to lead dioxide at the positive plate and spongy lead at the negative. Further innovations led to the idea of using a flat grid geometry for the base metal of the plate, and in 1881 Sellon[3] patented a grid which used an alloy of lead-antimony, and had a design intended to key the active materials in the grid mesh; both these features are still part of the basic design of many lead-acid storage batteries. Historical aspects of lead-acid batteries have been more thoroughly reviewed elsewhere[4-8].

I.2. Basic features of the lead-acid battery

The central structural elements are lead alloy grids which serve as framework and electrical contact to the positive and negative active materials. These active materials are formed after pasting the grids with a mortar-like mixture of lead oxides, sulfuric acid, and water, which is dried and cured in place, then electrochemically converted to the respective positive and negative active materials, lead dioxide and "spongy" lead. Microscopically porous separators are placed between each positive and negative plate to provide electrical insulation, while permitting ionic transport in the electrolyte between plates. A single "element" or "cell" is made up of a group of electrically connected positive plates interleaved with a group of electrically connected negative plates, effectively a group of electrode pairs connected in parallel. A number of "cells" connected in series constitutes a "battery;" since each cell produces an open circuit voltage of about 2 volts at full charge, a 12-volt battery has 6 cells, for example. Conductors, usually of lead or a lead alloy, are used to make the various electrical connections within the battery which lead to two external terminals. The cell elements reside in individual compartments in the battery container; the plates are usually located somewhat above the container bottom, to allow a space for collection of dislodged ("shed") active material sediment without causing inter-electrode short circuits, by resting on ridges in the bottom of the container or by being suspended from the wall or cover.

The lead-acid battery differs greatly in form, but not in principle, in the various battery designs used for different applications. Among these various applications are (1) automotive, or SLI (starting, lighting, and ignition), (2) industrial, or traction, (3) telephone, or standby, (4) submarine, (5) electric vehicle, and (6) load-leveling. The service requirements, particularly current vs. time history, differs greatly in these applications, causing some differences in materials problems and requirements. This paper will for the most part avoid lengthly discussion of the design distinctions between these various battery designs, which can be found elsewhere[4,5,8] and emphasize the basic principles of materials applications in the lead-acid system in general.

2

I.3. The lead-acid battery

The basic electrochemical reactions during charge and discharge may be expressed as follows.

At the positive plate:

(1) $PbO_2 + 4H^+ + SO_4^= + 2e^- \underset{Charge}{\overset{Discharge}{\rightleftarrows}} PbSO_4 + 2H_2O$, $E = 1.685 - 0.1182pH + 0.0295 \log a_{SO_4^=}$

At the negative plate:

(2) $Pb + SO_4^= \underset{Charge}{\overset{Discharge}{\rightleftarrows}} PbSO_4 + 2e^-$, $E = -0.356 - 0.0295 \log a_{SO_4^=}$
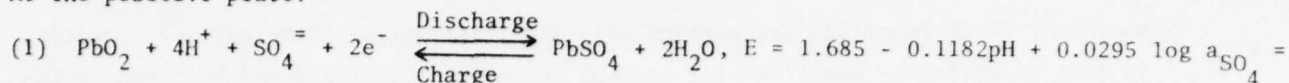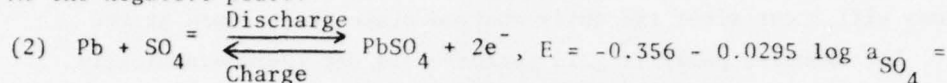
The potentials indicated represent values on an oxidation potential scale relative to the H^+/H_2 electrode as a reference (i.e., the reaction: $H_2 \rightarrow 2H^+ + 2e^-$ at $E_0 = 0.0V$). These two reactions can be abbreviated as the $PbSO_4/PbO_2$ electrode and the $Pb/PbSO_4$ electrode respectively (oxidized species on the right), occurring at applied relative potentials of about +1.66V and -0.35V on this scale (in 4 molar sulfuric acid). During discharge the (negative) lead electrode oxidizes to form lead sulfate, while at the (positive) lead dioxide electrode, PbO_2 is reduced to lead sulfate. Thus the negative plate is operating as an anode during discharge, giving up electronics to the external circuit and by electrical convention obtaining the designation of the "negative" terminal (yielding negative current, i.e., electron flow). Note that after charge, the essential chemistry of the system consists of the compounds PbO_2 (positive) and Pb (negative) at the electrodes, in a more concentrated acidic electrolyte, while at discharge the same compound, $PbSO_4$, comprises both electrodes, which are in an acidic solution which is more dilute on the average (and particularly dilute within and near the positive plate after rapid discharge). The limiting processes of the lead-acid battery are well known to be mass transport and ionic diffusion within the porous positive and negative electrode structures. These limitations will be discussed later in more detail when describing the active materials.

A total cell reaction can be expressed as:

(3) $PbO_2 + Pb + 2H_2SO_4 \underset{Charge}{\overset{Discharge}{\rightleftarrows}} 2PbSO_4 + 2H_2O$, $E = 2.041V - 0.1182 \, pH$
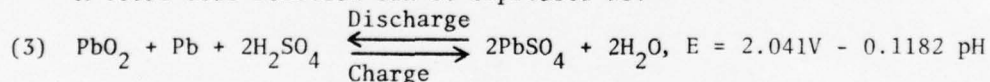
Other reactions of importance that may occur include possible "overcharge" reactions which will occur particularly after attaining the fully charged state of the electrodes (left side of equations 1 and 2). These include:

(4) $O_2 + 4H^+ + 4e^- \underset{Charge}{\overset{Discharge}{\rightleftarrows}} 2H_2O$, $E = 1.228 - 0.059 \, pH + 0.0147 \log p_{O_2}$

(5) $PbO_2 + 4H^+ + 4e^- \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} Pb + 2H_2O$, E = 1.355 - 0.1182 pH

(6) $H_2 \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} 2H^+ + 2e^-$, E = -0.059 pH - 0.0295 log p_{H_2}
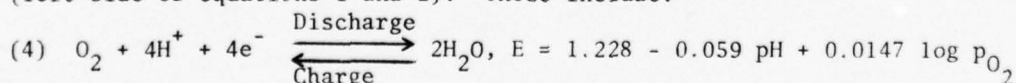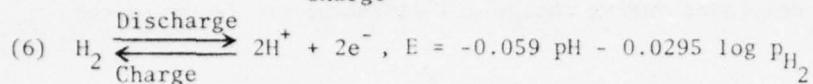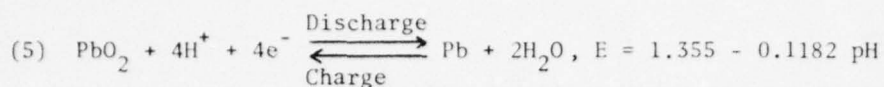
These last three reactions are particularly important during charging, i.e., reading right to left as written. Reactions (4) and (6) represent the oxygen and hydrogen evolution reactions for water electrolysis, while reaction (5) represents positive grid corrosion. These reactions will occur after the fully charged state is attained at the respective electrodes. For example, positive grid corrosion is not thermodynamically possible until all of the $PbSO_4$ in the plate has been converted to PbO_2 (although it may occur locally under various conditions) The reactions (4), (5), and (6) are irreversible; water and lead at the positive grid cannot be regained during discharge although under some conditions recombination of oxygen and hydrogen to form water can be obtained.

4

II. GRID MATERIALS

The positive and negative plates of a lead-acid storage battery are based on an electrically conducting lead alloy grid framework. These grids have two basic purposes. One is a structural role, the other an electrochemical role. The active materials of the plates are held in place by the mesh of the "grids," and current to and from the active materials is carried by them. Numerous grid geometries have been used to satisfy these purposes.[5] The specific lead alloys used for the grids are important with respect to both functions of the grids. Since the grids are exposed to the electrolyte, they participate in electrochemical action at both the positive and negative plates. The conjoint action of this electrochemical (corrosion) activity and the concurrent structural (load-bearing) role in the plate tends to both weaken them structurally and reduce their electrical conductivity. Therefore the primary properties of interest in grid alloys are yield strength and corrosion resistance, as well as such features as compatibility with the active material (adherence), castability, and electrochemical effects (see Table 1a). Currently, most battery grids are cast, rather than mechanically formed, but this situation may change in the future.

Strength is desirable in grid materials for two distinct reasons. First, during battery fabrication procedures, sufficient grid stiffness is required for efficient processing of the thin grids through such equipment as automatic pasting machines. Strength is also useful during battery service, as the grids most frequently bear significant loads (the active materials, their own weight, stresses due to corrosion); furthermore the typical service temperature of lead-acid batteries, more than half the melting point on a homologous scale, places the alloys in a regime where creep-type deformation is significant. The required strength is considered to be on the order of 40 MPa UTS. Pure lead has an UTS of about 14 MPa, while the highest strengths attained for lead alloys are in the range 65-85 MPa.

Corrosion resistance of the grids is also important for several reasons. First, it must be realized that penetration of any members of the grid constitutes an interruption of the most electrically conductive path in the battery; thus one of the primary mechanisms of capacity loss in these batteries is electrical isolation of certain volumes of active materials due to grid deterioration. Another aspect of grid alloy corrosion is the nature of the corrosion product formed; in this regard, the adherence of the active material and the electrical conductivity and reversibility of the product are important. Also, certain alloying and trace elements in the grid alloy composition may have significant effects on electrochemical processes in the battery.

With respect to castability, fluidity and resistance to "hot-tearing" (shrinkage tearing) on solidification are important. Several factors are influential on these properties and can be affected by alloying, including: the heat capacity, viscosity,

5

and surface tension of the liquid phase; the heat of fusion, width of the solidification range, solidification morphology, conductivity, and volume shrinkage on solidification. These factors have been discussed in detail by Heubner and co-workers[9-11].

Currently and historically, the most common lead-acid battery grid alloy systems are based on cast Pb-Sb and Pb-Ca alloys; there is also some use of pure lead grids in situations where low yield strength can be accommodated by grid or battery design innovations. The Pb-Sb and Pb-Ca based grid alloys will be discussed in detail. Other alloy systems of interest, pure lead, dispersion-strengthened lead, mechanically formed grids, and various innovative grid designs will also be considered. Table 1b summarizes current materials applied in grids.

II.1. Pb-Sb grid alloys

Lead-antimony alloys have historically been the most common grid alloy system, particularly in automobile-type batteries[5]. Antimony has typically been alloyed with lead in amounts ranging from 4 to 12 w/o Sb in battery alloys, with the average concentration tending to decrease in recent years for reasons which will be discussed. Pb-Sb is a eutectic alloy system and the microstructure of traditional battery alloy compositions consists of a dendritic network of primary lead solid solution surrounded by the eutectic phase mixture (see Fig. 1). The higher the Sb content, the lower the melting point, and castibility and mechanical properties are improved. Note that because of decreasing solid solubility with decreasing temperature for the lead-rich phase (from about 3.5% Sb at the eutectic temperature of 252°C to about 0.1 w/o Sb at room temperature), an age-hardening response is typically experienced after solidification of cast alloys[12-15], corresponding to the precipitation of fine-scale (10^{6} to 10^{10} plates/cm^{2}) particles of Sb on the {111} Pb planes[16,17]. The most desirable forms of this general microstructure are those in which the dendritic primary solidification structure is refined by the addition of alloying elements[11], or by increasing the cooling rate from the melt[19]; the more finely divided microstructures tend to yield more uniform grid corrosion behavior in battery service, as well as having inherently greater mechanical strength. Note that when the Sb concentration is reduced below about 3.5 wt %, as has been done recently for application in so-called "maintenance-free" or "low maintenance" batteries, the eutectic reaction does not occur, and only the simple precipitation situation exists.

Commercial Pb-Sb alloys currently utilize from 4 to 8 wt % Sb, and typically include small amounts of As (up to about 0.5 wt %), Cu (up to about 0.08 wt %), and Sn (up to about 0.5 wt %)[18,19]. Arsenic is considered to refine the typical Pb-Sb eutectic microstructure,[20] promoting more uniform corrosion[21-23] and enhancing castability[11]; it also is said to increase the age-hardening response which occurs subsequent to solidification[22-25]; arsenic has the undesirable side effect of being toxic, with the possibility

6

of arsine gas (AsH_3) being formed during service. Copper is also a grain refiner[11], and is said to improve the nature of corrosion and castabilty[11,26], and may tie up antimony and arsenic in precipitates such as Cu_2Sb and Cu_3As[27,28]. Tin has been traditionally added to Pb-Sb alloys to improve castability[10], and is considered to add a favorable solid solution strengthening effect; however, it has been shown to affect the aging response of cast alloys[29,30]. The corrosion and electrochemical effects of tin are in question[30-34]. It has been proposed that tin improves the character of the grid-active material interface, preventing formation of a passivating barrier film[35]. A great number of possible alloying additions to Pb-Sb alloys have been empirically evaluated, and several reviews of these alloying effects have appeared[6,7,28,36-38]. In all cases of alloying modifications to Pb-Sb alloys, the aim is to improve the grid alloy in one or more of the following categories: (1) mechanical properties, (2) casting ability, (3) corrosion performance, (4) reduced self-discharge. While the metallurgical aspects of grid alloying have been extensively studied, the battery electrochemistry aspects of such alloying are not as well characterized.

The use of antimony in lead-acid grid alloys has decreased in recent years due to certain undesirable electrochemical effects which are attributed to it. Batteries with Pb-Sb alloy grids, by their basic electrochemical nature, tend to have a relatively high overcharge current (the current passed by the battery at the end of charge); this overcharge current is proportional to the rate of water loss from the electrolyte via electrolysis. As a result of the consequent "gassing" of the electrolyte, at least two significant maintenance-related requirements arise: (1) periodic replenishment of water to the electrolyte is necessary (the familiar purpose of filler caps on traditional auto batteries); (2) corrosion of top-of-battery metal hardware (connectors and terminals), due to the acidic fumes which are created by the gassing. A further deleterious effect is that, in service, antimony tends to leach from the grid alloy and migrate to the negative plate, where it lowers the hydrogen overvoltage and leads to "self-discharge" of the negative plate[39-44]. Toxic stibine gas (SbH_3) may also be evolved during overcharge periods[45]. These effects tend to increase with service (charge-discharge cycling) and temperature.

On the other hand, there are apparently significant beneficial electrochemical aspects to the presence of Sb in the grid alloy, particularly relating to positive plate performance[46-48]. It has been suggested that Sb may have a role which improves the electrochemical activity of the positive active material. The presence of Sb also seems to improve the adhesion of active material to the grid[49] and the mechanical properties of the active material mass[46]. At present, the mechanism of antimony migration from the grid into the positive active material and subsequently to the negative plate is not fully understood, nor are some of the various effects on positive plate performance.

7

Because of the undesirable effects of Pb-Sb alloy grids, two basic engineering routes have been taken as alternatives. One approach is to simply lower the Sb concentration in the grid alloy (to 3 wt % or less); this is the partial solution utilized in so-called "low maintenance" batteries, which exhibit reduced water refill requirements and less battery terminal and connector corrosion. The other approach has been to eliminate Sb entirely, by utilizing another alloy base, most commonly Pb-Ca. This aviods entirely the deleterious Sb effects, but of course also eliminates the beneficial aspects. The tradeoffs involved in going to "low maintenance" (low Sb) and "maintenance-free" (no Sb) alloys have been reviewed by several authors[28,50-55]. It should be noted that when the alternative of low-Sb alloys is chosen, additional unique problems arise, involving a tendency toward coarse dendridic primary solidification, which gives rise to "hot tearing," coarse grains, and brittleness in castings[9,10,11,17]. Figure 2 illustrates casting shrinkage porosity which is accentuated near grid intersection points. The microscopic nature of hot tearing in the dendritic Pb-Sb microstructure is shown in Figure 3. These problems, which do not occur in conventional Pb-Sb grid alloy compositions, have been approached by utilizing fast cooling methods and by grain-refining alloying additions[9,11]. Figure 4 shows the microstructure of a low-antimony alloy which has been grain refined by the addition of Cu and S.

II.2. Pb-Ca grid alloys

Lead-calcium alloys have historically been substituted for lead-antimony alloys, particularly in certain battery applications[56-58] such as standby service (submarine and telephone batteries) and more recently in so-called "maintenance-free" automobile-type batteries[59,60]. Pb-Ca alloys have neither the unfavorable nor the favorable electro-chemical features of antimonal alloys. Therefore, their primary advantage is the elimination of the deleterious effects of Sb, while their main disadvantage relates to an inability to promote optimum active material performance a la Sb. This problem will be discussed in detail later on. Batteries with Pb-Ca grids can stand on open circuit or on "float" longer without the self-discharge problems of Pb-Sb batteries, and therefore can be used in M-F type batteries. At a given float voltage (2.17V is common for 1.210 s.g.) the float current is lower for a Pb-Ca battery than a Pb-Sb battery by as much as 4 to 10 times, because of the higher hydrogen overvoltage required for the Pb-Ca battery[53,61]. One of the bonus features of Pb-Ca alloys is that they are inherently more conductive than Pb-Sb alloys, which tends to improve battery efficiency in general, and raises the so-called "cold cranking rating" of a battery (the current which a battery at $0^{o}F$ ($-17.8^{o}C$) can deliver for 30 seconds and maintain a voltage of at least 1.2 volts per cell.)

8

Pb-Ca battery alloys derive from a precipitation-hardening region of the phase dia-
gram, with the maximum solid solubility of Ca in Pb being 0.10 wt % at the peritectic
temperature of 328°C and diminishing to 0.01 wt % at room temperature in this system.
Storage battery alloys usually contain less than 0.08 wt % Ca, in order to minimize a
unique corrosion growth effect which is related to the grain refining effect of Ca.
The typical microstructure, therefore, consists of essentially pure lead grains with
a dispersion of Pb_3Ca particles; this dispersoid is typically too small to be resolved
by light microscopy, but its presence is noticed indirectly by the irregular grain
shapes (see Figure 5). The distribution of the dispersoid, of course, depends on the
alloy content and thermal history, as for any age-hardening system, and for these
alloys, which are typically cast into grids, the cooling rate from the melt is quite
important. A rapidly cooled alloy will spontaneously age-harden at room temperature[62],
or may be accelerated by increasing the temperature above room temperature. From a
fabrication standpoint, melt fluidity is of importance in casting the typically very
thin battery grids, but the requisite melt superheat and mold pre-heating required for
satisfactory casting of Pb-Ca alloys are at odds with the desirability of rapid cooling
to obtain maximum age-hardening response. Pb-Ca alloys are typically softer just after
casting then Pb-Sb alloys, because they have not yet experienced the age-hardening res-
ponse that imparts most of their strength; this requires more careful handling of the
as-cast Pb-Ca grids.

Pb-Ca alloys have a tendency to non-uniform corrosion due to preferred grain boun-
dary attack. This leads to a swelling effect in the material due to growth of inter-
granular corrosion products, and gives rise to apparent "growth" of grids in service;
typically both the vertical and horizontal dimensions of a grid increase (see Figure 6),
an effect which increases with finer grain size[55]. This effect is apparently a conjoint
action, i.e., affected by both corrosion and mechanical stress, and creep-type deforma-
tion of the grid alloy is involved. The tensile strengths of cast Pb-Ca and Pb-Sb
battery alloys are similar, both being about 35-40 MPa; however, the creep strength of
cast Pb-Ca alloys is much lower, being about 0.6 kg/mm^2, vs. 2.0 kg/mm^2 for Pb-Sb, for
5,000 hrs. at 20°C.

Lead-acid standby batteries (including telephone, submarine, and load-leveling
applications), which often employ Pb-Ca alloy grids, are typically maintained in a fully
charged state by "floating" at a voltage slightly above the open circuit potential.
Under these conditions PbO_2 is the thermodynamically stable phase at the positive elec-
trode, so that there is a tendency for the grid to be corroded by oxidation to PbO_2.
Because the specific volume of PbO_2 is 21% greater than that of lead, the corrosion
product tends to induce stresses in the grid, particularly if the corrosion is grain
boundary localized, as for Pb-Ca grid alloys, and leads to grid growth and active material
cracking and shedding. For this reason, grain size control in Pb-Ca is quite important.

9

Measures that have been introduced to avoid the infavorable effects of float service on Pb-Ca grids include (1) operation at a slight ("trickle") discharge rate, with periodic recharges, to avoid positive grid anodization, and (2) utilization of pure lead grids. Another unique feature of Pb-Ca alloys is an apparent tendency to corrode on deep discharge in such a way that recharging requires an abnormally high applied voltage;[63,64] this effect has been attributed to formation of a passivating layer at the grid-active material interface[65-68].

As for the Pb-Sb alloy base, numerous alloying additions to Pb-Ca have been studied. The aim of Pb-Ca alloying in general is to improve (1) mechanical properties, (2) casting ability (reduced dross loss of calcium; increased melt fluidity), (3) reduced corrosion ("growth" of the positive plate), (4) reduced passivation (particularly after deep discharge). The most common alloying addition to Pb-Ca is tin, which is added below its solubility limit[59,60,69]. Favorable effects on the passivating film aspect of Pb-Ca grid corrosion are attributed to tin, as well as increased melt fluidity and improved strength, but claims of reduced dross loss of Ca due to the presence of tin have been questioned[69]. The effect of tin and other alloying elements in Pb-Ca alloys has recently been reviewed by Heubner and others[6,28,37].

II.3. Positive grid corrosion

Anodic corrosion of lead and lead alloy grid materials in sulphuric acid at various potentials has been widely studied[33,36,65.66,70-97]. While many of these studies have been performed on bare (unpasted) grids, they are still quite relevant particularly to the behavior of the positive grid during charge and float conditions. It has been shown that, in most circumstances, the thickness of the active material layer pasted on the positive grid has little effect on the thickness of the corrosion product formed on the grid[73]. Grid corrosion is important for several reasons. As the grid corrodes, its load-bearing, conductive cross-section decreases, and it becomes covered with a relatively loose, nonconductive layer of corrosion product such as lead sulfate. Furthermore, in the conversion of the grid to higher specific volume corrosion products, stresses may be transmitted to the active material mass or to the grid itself, leading to active material "shedding" or "grid growth" respectively.

While it is desirable to minimize the corrosion penetration rate of the grid, it is not desirable to completely passivate the surface, as this will interfere with current passage. It has been suggested that the problems of capacity loss after float or cycle service, and difficulty in recharging after deep discharge, could be related to barrier film effects[63,65,66]. This is a particular problem with Pb-Ca battery grids, sometimes referred to as "sulfation." The term "sulfation" is used in several senses relative to lead acid batteries. In a general sense, it means the formation of lead sulfate from

10

the active materials during discharge. It is also used to refer to the product of
local action self-discharge reactions on the electrodes; the lead sulfate formed by
such processes, while the battery is in the charged condition on open circuit, tends
to consist of larger crystals and is more difficult to completely reconvert on charging.
The term is also used to refer to excessive lead sulfate formation due to various causes,
such as allowing the battery to stand in the discharged condition, or using too highly
concentrated electrolyte. This type of sulfate formation is most difficult to recon-
vert, requiring longer times and higher voltages to break down the compact crystal layers.

Pure lead placed in sulfuric acid without an applied potential will tend to become
passivated by a layer of insoluble lead sulfate; thus lead is inherently corrosion-
resistant under these open-circuit conditions. In fact, because of the resistive nature
of the film which is formed on open circuit (a condition which is very relevant since a
battery is often on open circuit), an overpotential is required to reduce the film from
the surface by an applied negative potential[7]. Of course, under the influence of
applied anodic potentials, such as occur during charging, corrosion will proceed further
than under open circuit conditions, and a more extensive anodic corrosion film will
develop. The anodic corrosion products formed on bare lead in sulfuric acid are a
sensitive function of pH and potential [7,74-76,94,97]. Compounds formed with increasing
oxidation potential are $PbSO_4$, PbO, α-PbO_2, β-PbO_2[7,74,88] corresponding to increasing
applied charge voltage to a battery. A very complete discussion of conditions and
mechanisms for the formation of various corrosion product compounds is given by Burbank
and others[7,94].

With regard to alloying effects on corrosion behavior of the grids, one of the most
important effects relates to microstructure[76-79,81,85,87]. Features such as grain size,
compositional segregation, precipitate distribution, etc. can be changed drastically by
alloying. In addition, certain alloying elements may participate in favorable or unfav-
orable electrochemical reactions, for example by raising or lowering the overpotential
for hydrogen or oxygen evolution (reactions (4) and (6) respectively), or by changing in
some way the equilibrium potentials for other reactions. These electrochemical effects
have been reviewed by Burbank et al[7] and will not be restated here. Although extensive
empirical data is available, little of a fundamental nature is presently known about
the role of alloying elements in grid corrosion and electrochemical processes. Various
mechanisms by which certain alloying elements inhibit grid corrosion have been proposed.
These include explanations that can be considered either electochemical or microstructural.
For example, the favorable effect of Ag additions to Pb-Sb alloys has been attributed
variously to: (1) prevention of shedding of a compact PbO_2 protective layer next to the
grid[98]; (2) lowering of the oxygen overvoltage at the positive electrode, therfore re-
ducing the corrosion rate under constant current overcharge conditions[83,99]; (3) catalytic

11

activity in decomposing the powerfully oxidizing persulphate ion, thus indirectly preventing the formation of more PbO_2 from $PbSO_4$[100]; (4) spheroidization of the interdendritic eutectic phase mixture, which is coated by Ag segregation, therefore making the preferentially attacked microstructural regions discontinuous and protected[79]. Among the alloying elements considered generally favorable from the standpoint of grid corrosion resistance are Sb, As, Ag, Cu, Te, Ni, Tl, Co. Note that some of these elements may be unfavorable from other viewpoints. Among the alloying elements universally considered unfavorable are Fe, Bi, Zn, Li.

From the microstructural viewpoint, corrosion of alloys with a single phase grain structure (such as pure lead) or with fine precipitate particles in a matrix of parent phase grains (such as Pb-Ca or dilute Pb-Sb alloys), tends to proceed preferentially along the grain boundaries. This mode of attack is associated with the "grid-growth" problem mentioned earlier. The grain size of Pb-Ca alloys is a sensitive function of composition, with finer grains for higher Ca content. The activity of these boundaries is nearly independent of grain size, so that the Ca content is usually kept below about 0.07 wt% in order to avoid very fine grains. "Pure" lead, on the other hand, suffers more corrosion for coarse grains than fine grains, apparently because of higher concentrations of grain-boundary segregated impurities in the case of lower total grain boundary area per unit volume[77]. Corrosion of Pb-Sb alloys with a eutectic microstructure proceeds by preferential attack of the eutectic[68,90,101]. Because of the relatively fine scale of this structure, Pb-Sb alloys tend to corrode more uniformly than pure lead or Pb-Ca alloys. For this type of microstructure, the finer the microstructure, the more uniform is the attack, so that microstructure-refining alloying additions such as As and Cu are desired. Similarly, when the segregation of certain alloy impurities to interphase boundaries is considered detrimental, as it is in Pb-Sb, an increase in the number of such boundaries is considered desirable to more widely distribute the element and thus dilute its local concentration at any given point[77].

II.4 Other grid materials

In addition to traditional Pb-Sb and Pb-Ca based alloys, numerous other lead-based alloys have been empirically evaluated, but few satisfactory alternatives have been found; several reviews of this subject have appeared[28,32,36-38]. Patents have been issued at one time or another for alloys of lead with As, Sn, Ag, Co, Cu, Si, Ce, Al, Li, Cd, Tl; in fact virtually every miscible, low-melting element has been investigated for grid alloy application. In some cases the development of new lead-based materials has been coupled with new fabrication methods, new grid designs, or even new battery designs. Dozens of innovative grid designs and materials have been reviewed in Lead Abstracts in the last few years; most of these are based on recently granted patents,

and do not necessarily represent successful schemes. These innovations can be grouped in several general categories: (i) non-traditional lead alloys developed for application in the traditional grid geometry, (ii) non-traditional methods of fabrication of grids from traditional and newly developed lead alloys, (iii) non-lead and non-metallic materials utilized as a base grid structure, coated with layers of conductive and active materials, (iv) schemes which are distinct deviations from the traditional grid geometry. Many of these schemes are aimed at improved active material utilization, or greater energy or power densities. The latter is important since one of the major sources of battery weight is the grids, which are not intended to participate in the cell reactions, i.e., are not active material.

(1) Pure lead

While it may seem inappropriate to consider the use of pure lead as an innovation, nevertheless pure lead is one of the few alternative "alloys" that has been successfully applied in recent commercial designs. Two examples which will be cited here represent the use of non-traditional materials together with unique designs developed specifically for those materials and the application. The primary features of pure lead are that it has virtually no adverse electrochemical side effects, has good corrosion properties in terms of cyclic and float service, but has extremely low strength. The last factor means that pure lead satisfies the conductive but not the structural role of a conventional grid. Pure lead grids have been applied recently in a unique cylindrical telephone battery design[103,104] using a novel horizontally-oriented, circular-shaped grid[105,106]. The grid growth problem is controlled by appropriate geometrical design of the grid so that contact is continuously maintained with active material, and capacity actually increases with time. Because of the low strength of pure lead, conventional thin-grid designs could not be used, so a self-supporting structure was designed, with grids which individually have a shallow cone profile, stacked horizontally like pancakes. Of course this design does not produce exceptional energy density, but provides extremely long life (30 years or more estimated), which is most important for the application (standby telephone service).

Another unique battery design utilizing pure lead electrodes was recently developed as a sealed, high energy density, high power, (1.47 watt-hrs/cm^3 or 12.6 watt-hrs/lb.) system for standby applications in D and X size 2 volt cells[107]. The design in this case involves spirally-wound, thin, pure lead grids with positive and negative active material separated by a porous fiberglass strip. This assembly, not dissimilar from Planté's original battery, creates a tight package that is kept together by being pressed tightly into a cyclindrical polyethylene case. The cell is able to be completely sealed (no vents) without risk of gas pressure buildup because of a delicate positive-to-negative electrode balance that is struck, by which the positive becomes fully charged before the

13

negative, so that oxygen is produced first, then carried to the negative where it is recombined, so that the negative does not charge any further and water is not lost during overcharge. This is a unique "maintenance free" concept, unlike that used for conventional so-called maintenance free batteries, which simply try to reduce water electrolysis to a minimum and provide enough excess electrolyte to last until the battery fails by other means of deterioration. Because of the use of pure lead, corrosion and contamination problems are minimal, and long life under float conditions of 2.3 to 2.4V is possible[108].

(2) Dispersion-Strengthened (DS) Lead

Dispersion-strengthened lead has received major attention for use as grids[108-117], but has not yet been successfully applied in batteries. This material is usually derived by powder metallurgy/mechanical working processes, and so has the advantages of a non-pyrometallurgical fabrication method and outstanding mechanical properties (up to 60 MPa yield stress). It also has higher conductivity than conventional grid alloys (about 20 μohm-cm vs. 24 μohm-cm for Pb-Sb alloys) and does not contain antimony. Most commonly, submicron-sized lead oxide (PbO) particles have been used (1 to 5% by volume) as the dispersoid, although other dispersoids have been investigated, including Cu[117-119], Al[117-119], Ag[120], Ni[121,122], Al_2O_3[117,123-125], $BaSO_4$[126], AgO[127], SiC[128], and refractory metal compounds such as WC, TaO, WB, or TiC[127,128]. Following consolidation of the composite by powder metallurgy or other techniques, the compact is mechanically fabricated by processes such as rolling, drawing, forging, and stamping. This creates a very fine scale microstructural distribution of strengthening particles and dislocation substructure, and these materials have obtained some of the highest strengths reported for materials based on a lead matrix[114,115].

Among the disadvantages of DS lead are loss of its desirable as-worked microstructural features during fusion joining processes[114,115,129], as well as higher cost. Of less significance are its anisotropic properties. Plates using these grids have shown irregular cycle life in batteries[108] and a tendency to active material shedding due to inferior adherence to a smooth-surfaced wrought grid[105]. Corrosion rates are typically higher than for pure lead[116], as might be expected for a material with such a high degree of stored internal energy.

(3) Thermomechanically processed alloys and alternative fabrication methods

Dispersion-strengthened lead[110-112,117], as well as various lead alloys, have been investigated in specific association with mechanical-thermal fabrication methods. Among these are Pb-Sb[16,130-133], Pb-Ca-Sn[55,60], and Pb-Cd-Sb alloys[134,135]. Contrary to views held in the past, it has been shown that lead alloys can have stable strength increases imparted by appropriate mechanical-thermal processing. Care must

14

be taken, of course, to avoid spontaneous recrystallization, since room temperature represents about 0.5 Tm on a homologous scale for most lead alloys, and an even higher fraction during service. These temperatures also encourage significant creep-type deformation processes to occur[27]. Development of stable subgrain dislocation structures by appropriate processing has been shown to be possible in lead alloys[134] and should be quite effective in increasing the creep resistance, as it has in numerous other alloy systems. Figures 7 and 8 illustrate, for thermomechanically processed Pb-Cd-Sb, the longitudinal cross-section, and the substructure developed, respectively. This type of microstructure becomes particularly creep resistant when a finely-dispersed second phase is present to stabilize the subgrain dislocation structure.

Other developments[136-138] in search of an alternative to conventional grid casting have included casting techniques such as continuous casting and rapid pressure casting, and mechanical fabrication methods such as punching, stamping, and expanding (see Figure 9). A direct continuous sheet casting process for lead alloy sheet, with the grids then fabricated mechanically from the sheet, has been developed to the point of actual application; this process involves rotation of a cooled casting drum through a molten lead alloy bath, with the gauge and as-cast microstructure controlled by appropriate balancing of the heat transfer parameters, including drum and bath temperature and drum speed[137,138].

(4) Coated grid substrates

Some of the patented schemes that have recently been proposed for coated grids include: steel base/nickel plating/PbO_2 electro deposit[139]; aluminum base/zinc deposit/silver plating/lead deposit[140]; plastic base/hot dipped lead coating[141]; titanium base/PbO_2 electro deposit[142]; nickel-tantalum alloy base/gold plating/PbO_2 electrodeposit[143]; titanium base/gold or lead plating/PbO_2 electrodeposit[144]; etched nickel substrate/PbO_2 electrodeposit[145]; copper base/lead coating. These schemes are generally aimed at decreasing grid resistivity and grid weight, which are important particularly for high power and high energy density batteries. Of course, the fabrication complexity and costs are much higher than for conventional grids. However, the major disadvantage of many of these schemes is the introduction of a new active species, such as a new metal, into the electrochemical system. This seems to almost always have some undesirable result, and for this reason the use of coated grids of metals other than lead has generally been discouraged. For example, titanium, when used in sulfuric acid solutions, tends to form a passivating oxide film over its surface[146]. Therefore, in order for the grid to maintain its conductive function, either this oxide must be reduced or a conductive coating applied to the grid. Most such schemes prove to be limited in cyclic life, since whatever coating initially covers the titanium eventually breaks down and re-exposes it to the electrolyte. Similarly, in the use of copper as the base metal for lead-coated grids, the inevitable exposure of copper to the electrolyte has adverse electrochemical

15

effects on battery performance, especially due to local cell formation on the electrodes, with self-discharge and other unfavorable effects.

(5) Innovative plate designs

Numerous non-traditional plate designs that consist of unique composite material structures have been proposed; most of these are intended to improve active material utilization and retention, or to reduce weight, improve conductivity, etc. Examples of various innovative grid designs and fabrication methods are shown in Figure 9. Some of the more recently patented schemes include: short carbon fiber bristles attached to a rectangular network pattern of twisted lead alloy wires[147,148] (Figure 9i); a fan-like pattern of lead wires interwoven with a linear pattern of plastic filaments (Figure 9g), a scheme that reached commercial application[149]; a non-conductive base spread with paste and then coated with a conductive layer consisting of glass fibers and lead[150]; perforated lead foil sandwiched between porous composite sheets which consist of synthetic fibers (such as polypropylene or polyethylene) and active material, these layers fabricated by paper-making type machinery[151]; grids consisting of intersecting current-carrying separators[152]; plates made from pressed lead fibers, with the periphery and other areas hard-pressed to create structural integrity, and these areas coated with a film of synthetic resin while the rest of the plate is formed[153]; a fibrous composite strip material consisting of lead or lead-coated fibers, divided into a grid pattern by stenciled network pattern of synthetic resin lines applied to the surface[154]; titanium sheet sandwiched between open-mesh expanded titanium grids, with active material pressed into the openings[155]. It is obvious that fabrication procedures for these designs are often more complex and expensive, and service performance is unproven in many cases, to be expected to vary widely depending on the specific design. Note that plastics have been employed in various ways in innovative grid designs. In some cases, plastic frameworks have been electroplated with lead, while in other designs, lead conductors have been in some way interwoven with plastic networks (Figure 9g). Generally, these designs offer the advantage of decreasing the total grid weight contribution to the battery, increasing the energy density.

16

III. ACTIVE MATERIALS

The solid materials which undergo chemical reactions to produce or absorb energy during discharge or charge of a storage battery are known as "active materials." The positive and negative plate grids of a lead-acid battery are initially filled with a "paste" which, by charging, is intended to be converted to the respective active materials, PbO_2 at the positive plate and "sponge lead" at the negative plate. The initial paste mixture consists of lead oxides (mostly PbO, "litharge"), sulfuric acid, and water, as well as other associated compounds and trace elements. The oxides are introduced into this mixture in powdered form, typically <300 mesh (about 50 μm maximum particle size), so that the paste, when cured, dries into a rigid but highly porous mass, so that electrolyte may pass. The negative plate paste mixture also typically includes so-called "expanders" to prevent a tendency for the sponge lead to contract to a dense mass during cyclic service. The specific paste mixture and pasting/curing processes are unique for a given battery brand and type, and are different for the positive and negative plates. Generally speaking, the dry powder introduced into the paste is intially a mixture of Pb, PbO and Pb_3O_4. When mixed with sulfuric acid and water, complex chemical reactions give rise to a paste generally composed of Pb, PbO, $PbSO_4$, Pb_3O_4, $PbO \cdot PbSO_4$, $3PbO \cdot PbSO_4 \cdot H_2O$ (tribasic lead sulphate), and $4PbO \cdot PbSO_4$ (tetrabasic lead sulphate). The exact composition depends on numerous factors, such as starting mixture, rate of mixing, temperature, etc. The major compounds are ususally one of the basic lead sulphates and PbO.

After pasting, the plates are generally cured over a period of days in a humid atmosphere, and additional chemical reactions occur. The aim is to develop and maintain the most rigid active material mass possible; this is promoted by interlocking of the crystallites of the compounds formed during pasting, curing, and forming. After pasting and curing, the plates are "formed" by current passage to create the respective active materials, PbO_2 and Pb. At the fully charged condition the positive plate appears to the eye as a rich dark brown granular mass, while the negative plate has a gray color. During battery service the active material of either electrode must remain: (1) electrically conductive, (2) mechanically cohesive, (3) physically porous, (4) electrochemically active (see Table 2).

The other electrochemically active entity of the battery system is, of course, the electrolyte, which for the lead-acid battery is a dilute solution of sulfuric acid. The electrolyte of a fully charged automobile-type battery contains about 35% sulfuric acid by weight or about 24% by volume; this corresponds to a specific gravity of about 1.265 at 80°F (26.7°C). During discharge, the specific gravity decreases continuously, reaching a value of about 1.120 at full discharge. Therefore, specific gravity can be used as a rough indicator of the "state-of-charge" or remaining capacity in a battery.

17

The electrolyte used in certain types of standby service, such as telephone batteries, or where there are low discharge rates, tends to be less concentrated (lower specific gravity) than that used in high-rate discharge situations such as SLI batteries. For example, at full charge, the specific gravity of the electrolyte for a typical telephone battery may be about 1.210, for a typical SLI battery 1.265, and for a typical submarine battery 1.285. Higher concentrations are used in high rate situations because of the mass transport limitations of the system, as high discharge rates tend to more rapidly dilute the acid locally, in the vicinity of reaction sites in the positive plate. However, higher concentrations also tend to accelerate grid corrosion and accentuate passivation problems.

Two of the classical problems in lead-acid batteries are briefly described as follows: (1) The battery typically has maximum capacity just after initial forming/conditioning, and decreases with subsequent discharge-charge cycling. (Note: An exception to this often occurs in Pb-Sb batteries, where the capacity may increase continuously for some time before decreasing). (2) A battery maintained on "standby" status at a float voltage (just above full charge voltage) will, when called on to discharge, produce less capacity than prior to the float exposure. These problems can be briefly referred to respectively as the "cycle-loss" and "float-loss" capacity problems. Much of the research toward improved active materials and grid materials relates to one or both of these problems. In terms of realizing capacity, most contemporary lead-acid batteries are "positive-limited," i.e., reach a fully discharged state when the capacity of the positive plate is exhausted, while the negative plate at that point is not fully discharged. Most of the current efforts to improve the lead-acid battery relate to the performance of the positive plate.

III. 1. Positive active material

It is useful to discuss the positive plate in view of several specific mechanisms that have been proposed for loss of capacity, including the following: (1) formation of a barrier grid corrosion film at the grid/active material interface, which because of its highly resistive nature, prevents full current withdrawal on discharge; (2) decreased total surface area of active material due to morphological changes; (3) active material encapsulation by local surrounding nonconductive compounds during charge or discharge; (4) active material isolation in certain volumes of the plate, due to grid corrosion; (5) active material shedding, i.e., actual physical loss from the plate, due to grid corrosion and growth and other factors; (6) active material softening and loss of contiguity, including loss of interparticle contact and therefore loss of electrical contact; (7) conversion of active material to an electrochemically inactive form. It must be stated at the outset that in spite of the extended period of existence of this system,

18

no clear explanation is presently available for the decrease in capacity with cycling of these electrodes. In view of these various possible failure mechanisms, several general features of the positive active material are obviously important, including the mechanical stability of the active material mass, the microscopic morphology of the plate, the chemical or electrochemical "activity" of the compounds present, and adherence of the active material to the grid.

The morphological features of the particles of compounds used or evolved in the initial paste mixture are of great importance, particularly with respect to the mechanical stability of the as-pasted, as-cured, and as-formed active material mass on the grid. The overall plate morphology is also of great importance relative to capacity and mechanical stability during service. The microstructure of battery plates has been studied by cross-sectional optical microscopy[72,156] and replica electron microscopy[46,157-160]. More recently, study of the morphological forms of the active material of both positive and negative plates has been greatly aided by the use of scanning electron microscopy[161,162]. These studies have made it possible to recognize the various compounds by external shape and other means, and therefore to follow the mechanisms of reactions occurring during curing, forming, and discharge-charge cycling. Figure 10 shows the typical structure of the as-formed positive plate active material: Notice that the shape of the original litharge particles are still evident in the PbO_2 morphology. It is important to note that one fact which is clear from microstructural studies of battery plates is that the microstructure is a function of the chemical/electrochemical history of the electrode, i.e., the paste mixture, curing and forming conditions, and charge-discharge history all contribute to the resultant microstructure. One cannot simply refer to the microstructure of a "charged" or "discharged" electrode, for example, without indicating this history.

For example, if a plate is pasted and cured to form $3PbO \cdot PbSO_4 \cdot H_2O$ as the major as-cured compound, the structure of a fully formed positive plate consists of rather equiaxed dipyramidal crystals of β-PbO_2 with about 1 μm maximum size[157]. Positive plates in which the as-formed active material is made up of equiaxed PbO_2 particles tend to soften and fail more rapidly than plates made up of prismatic PbO_2 needle crystals, which better retain a rigid structure[159]. It has been shown that the tetrabasic lead sulphate, $4PbO \cdot PbSO_4$, is the preferred as-cured chemical compound for creation of a mechanically rigid mass of β-PbO_2 during plate forming[49,163,164]; $4PbO \cdot PbSO_4$ crystallizes as large elongated prisms, and anodizes during forming to a morphologically similar form of interlocking prismatic needle crystals of β PbO_2.

It has been observed that with repeated cycling, the initially granular PbO_2 formations in the positive plate evolve into more consolidated masses within the active material volume[47] (see Figure 11). Eventually, a structure develops which has been dubbed

19

"corraloid" by Simon and co-workers[161]. As seen in Figure 12, this structure encloses relatively large open spaces within the plate volume, and therefore represents a much-reduced total surface area for the active material mass. It is reported that this corraloid structure eventually breaks up, leaving a nondescript mass of loosely con-nected particles, at which point the electrode has lost most of its capacity[161]. It is not yet clear exactly what role the corraloid structure plays relative to battery per-formance, or whether this structure is a typical development in positive plates. From the standpoint of structural rigidity, electrical conductivity, porosity, and active surface area, this structure would appear to be quite favorable to electrode performance. It has been determined, however, that the electrode is losing capacity even as this structure develops, suggesting that the loss in capacity must be related to some other, perhaps more subtle, change in the electrode[161]. Among the possibilities are formation of a barrier corrosion layer of some kind at the grid-active material interface, or in-creased structural transformation of PbO_2 to a more electrochemically "inactive" form.

Recent work[165] has given evidence that a layer of resistant $PbSO_4$ crystals tends to develop with cycling, and remain after recharging, incompletely converted, at the grid: active material interface (see Figure 13). This type of sample was prepared for examination by breaking the active material away from the grid, so that $PbSO_4$ crystals at the interface may remain on the grid surface or be taken away with the active material. Figure 13b shows a region where only one, partially converted, sulfate crystal remains, and the imprint of other crystals is seen in a network of fine dendritic PbO_2 on the grid active material surface. Figure 14 shows the nature of this dendritic network in more detail; extremely fine, needlelike crystals of PbO_2, apparently formed as the result of a dissolution-precipitation process from the $PbSO_4$ crystals, develop a continuous micro-scale network. This network extends throughout the active material mass tending to be-come more developed with repeated cyclic transformation of the compounds[166]. Note that this network structure is a microscale feature only within the active material masses in the plate, and does not extend throughout larger-scale openings as within the "corraloid" structure. This network structure is considered to be a favorable microstruc-tural feature, providing both conductive and structural connectivity with the active mate-rial.[166] Attempts have been made to artificially impart similar structural and conductive properties into the positive active material, such as by the use of fine-scale carbon-fibers[147,148]; Figure 15 shows the structure of discharged active material containing carbon fibers that serve, on discharge, as nucleation sites and support for precipitated lead sulfate crystals.

An important aspect of the cycling of positive plates is that a 57% increase in volume is involved in converting from βPbO_2 to $PbSO_4$ (molar volumes 27 · 9 cm^3 and 43 · 8 cm^3 respectively). These changes in volume can be critical, because they may

lead to development of internal stresses in the plate and promote active material shedding.[167] Relative to this, paste mixing can be critical. For example, in the limit a so-called isovolume mix of tetrabasic lead sulphate, $4PbO \cdot PbSO_4$, and litharge, PbO, can be used, such that there is no volume change during forming (referred to as a "stable" active material), which therefore will increase cycle life. However, such an isovolume mixture will tend to, of necessity, be higher in density, which means that there will be lower porosity and total active surface area, and therefore decreased utilization of active material and lower capacity. Thus it is seen that in terms of the paste mixture, cycle life and capacity are at odds with one another. At the same time, it has been observed by direct microscopic study that the total volume occupied by a $PbSO_4$ (+ associated void space) structure can be less than that occupied by a PbO_2 (+ associated void space) structure, even though the specific volume of the $PbSO_4$ compound is greater than that of PbO_2. Therefore, no residual stresses necessarily are associated with phase transformations in the active material mass itself. As mentioned earlier, the repeated cyclic transformations between PbO_2 and $PbSO_4$ are believed to occur entirely via dissolution-precipitation reactions, rather than by solid state reactions.

Two crystalline polymorphs of PbO_2 are known, orthorhombic α-PbO_2 and tetragonal β-PbO_2[168]. An additional, amorphous, form has been suggested, along with other crystalline modifications[169]. A charged positive plate consists almost entirely of β-PbO_2[7]. During formation of the positive electrode, the outer layer of anodic corrosion product has been identified as primarily β-PbO_2, while an inner layer closer to the metal is primarily α-PbO_2 frequently intermixed with β-PbO_2[88,157]. Both forms of PbO_2 will discharge to $PbSO_4$, but α-PbO_2 discharges at a slower rate[90]; on cycling, the amount of α-PbO_2 will gradually decrease in the areas away from the grid; however, α-PbO_2 will continue to be generated by corrosion of the grid metal[90].

Positive battery plates cannot be fabricated by directly pasting the grids with chemically prepared PbO_2, for this proves to be an electrochemically inactive form, i.e., will not undergo the desired electrochemical reaction, $PbO_2 + 4H^+ + SO_4^= + 2e^- \rightarrow PbSO_4 + 2H_2O$, in order to produce capacity. Rather, the PbO_2 active material must be formed electrochemically by charging the paste mixture of lead oxides and sulphuric acid, i.e., essentially by carrying out the reverse of the reaction written above. Simon and Caulder of NRL have hypothesized that an inactive type of PbO_2 forms in increasing amounts during charge-discharge cycling[170], leading to decreases in capacity. Experimentally, it has been found that the "active" and "inactive" types can be discriminated using DTA, thermogravimetric analysis, high temperature mass spectrometry, and pulsed NMR[169,170]. Chemical and x-ray spectroscopy, x-ray diffraction, and morphological examination cannot distinguish between the two types. The mechanism by which the inactive type forms, and the explanation for its ineffectiveness in reacting to form lead sulphate

during discharge are not completely known. Considerable microscopic work has been done to attempt to deduce the sites in the active material mass where these types occur[72,161]; this work has suggested that during discharge, particles of the inactive form of PbO_2 are characteristically deposited at the surfaces of lead sulphate crystals, and serve as nuclei for crystals of the active form during recharge. Whereas the mechanism of formation of inactive PbO_2 is not completely clear, it would seem that, if such an inactive form does exist, it might form by chemical oxidation of $PbSO_4$ during periods of battery inactivity, or at insulated areas in the active material mass.

PbO_2 typically exists with a non-stoichiometric defect crystal structure, with compositions deficient in lead, the proportion of oxygen ranging from 1·98 to 1·85. This defect structure naturally allows various foreign ions to be incorporated, and the presence of water and/or elements of water in the PbO_2 crystal structure has been shown[170], and pulsed NMR studies have shown that a short period relaxation, probably associated with the presence of protons (H^+) or hydroxyl ions (OH^-), tends to disappear with battery cycling. Thus, it has been hypothesized that certain cycling-associated effects, such as loss of electrochemical activity, and tendency toward active material shedding, are related to the structural features which accompany the short period relaxation effect, i.e., there may be a tendency for the PbO_2 to revert to a more defect-free, but less electrochemically active, structure as cycling continues, due to a migration of foreign species from the defect structure.[161]

Besides the historically central problem of capacity-loss in service, there is the more fundamental problem of active material "utilization." Typically, only about 50-60% of the active material in the positive plates of contemporary batteries is utilized in terms of producing energy via participation in electrochemical reactions in the battery. Increases in this utilization parameter and improvements in capacity retention will both be related to the fundamental effects of innovations in paste composition, paste preparation, particle size, and curing and forming operations, i.e., the chemical/electrochemical history of the fabricated plate. Basic parameters that affect utilization include the related, and history-dependent, parameters of porosity and total active surface area. As noted previously, the rate-limiting processes associated with the lead-acid battery system are related to mass transport and ionic diffusion within the porous structure of the respective electrodes[171,172]. For example, considering the positive plate, the physical result of the discharge reaction is to deposit crystals of $PbSO_4$ on the surface and within the pores of the as-charged PbO_2 structure, and simultaneously dilute the adjacent electrolyte; this crystal deposition tends to cause a decrease in the average pore diameter, and so interferes with the access of fresh electrolyte to active material within the plate. Considering these rate-limiting features, there are obviously basic compromises that must be made between utilization, absolute capacity, and high-rate energy release.

22

III.2. Negative active material

The "spongy lead" of the negative plate, which is formed by reduction of $PbSO_4$ on each battery recharge, is a very ductile material, which tends to coalesce and densify. Figure 16 illustrates the structure of as-formed negative plate active material; evident are the outlines of the original litharge crystals from which the spongy lead formed; on a fine scale, the active material masses consist of groups of individual acicular lead crystals. If a negative plate were formed from a paste of litharge (PbO) only, it would lose capacity rapidly, and the active material would shrink and crack. In order to prevent this, so-called "expanders," such as powdered $BaSO_4$, acetylene, and carbon black, have historically been added to the negative paste mixture to extend cycle life[173-175]. The essential benefits of negative plate additives are effected during charging, by maintaining a favorable active material structure, but realized during discharge, where the sponge lead active material reacts to form $PbSO_4$. A porous active material mass is necessary to allow the negative plate to be as fully discharged as possible. Otherwise, the battery will be "negative-limited" in the sense that if the negative electrode cannot complete its half-cell discharge reaction, then the positive electrode cannot operate either.

Recently, considerable more sophistication has been introduced into the development and selection of negative plate additions. Many years ago, when wood separators were widely used (see next section), it was noticed that negative plates deteriorated less than with more inert separators, suggesting that some beneficial elixer was extracted from the wood. This initiated the addition of substances such as raw wood flour, "lignin" (purified and dried wood flour), and related complex surface-active agents such as ligno-sulphonates. There are currently three basic classes of organic expander, namely alkali lignin, lignin sulfonic acid (LSA), and desulfonated LSA. The mechanism of organic expanders such as lignin, and additives such as $BaSO_4$, on the performance of the negative plate has now been systematically studied[176-178], including examination by direct microscopic examination[179,180]. It has been found that when lignin is present in the paste it modifies the structure of lead crystals that grow during the formation process, producing smaller crystals with a more porous structure and greater surface area[179-180]. These smaller lead particles, in turn allow more complete conversion of their volume to $PbSO_4$ during discharge, i.e., tend to be more completely converted before a thick barrier film of $PbSO_4$ can form[179]. Lignin also produces a difference in the manner of deposition of the lead sulfate crystals, giving a finer, more porous crystalline deposit[179]. It has been proposed that barium sulfate is beneficial to the negative plate because it provides a surface on which lead sulfate deposits preferentially, and so prevents lead sulfate from coating and passivating the sponge lead surface. It has also been shown that the organic expander deposits on the lead surface, and similarly prevents lead

sulfate passivation. The actions of organic expander and $BaSO_4$ are considered to be synergistic[180]; therefore, currently both materials are typically used together.

Recently, polymer-bonded negative paste has been studied, based on an initial mixture of PbO, carbon black, and a solution of neoprene in toluene, with claims of superior cycle life, charge acceptance, and lack of gassing compared with conventional pasting of Pb-Ca-based alloy grids (Pb-0.06%, Ca-1%Sn)[181]. Figures 17 and 18 show the discharged structure of polymer-bonded negative plate active material after long cyclic service.

24

III. 3. Additives and impurities

Numerous additives to the positive active material have been suggested and studied in an attempt to develop and maintain high capacity in the positive plate. The favorable aspects of antimony in the positive plate were mentioned earlier. The exact mechanism for these effects is not known, but antimony apparently helps preserve large surface area, small particle size, and structural integrity in the positive active material mass[46,67]. It has been shown that differences in active material composition, such as a larger percentage of α-PbO_2 in the as-formed plate, and differences in morphology, such as more prismatic crystals, are favored by the use of antimony-containing grid alloys[46]. Antimony is also claimed to somehow assist in the bonding of β-PbO_2, the majority as-formed compound, to the grid, perhaps via improved bonding between β-PbO_2 and the α-PbO_2 corrosion layer near the grid[88].

Besides the favorable effects of antimony at the positive plate, certain unfavorable effects at the negative plate occur[41-43,45], as discussed earlier. Antimony migrates from the positive plate to the negative, deposits on the negative plate, and lowers the hydrogen overvoltage, giving rise to increased hydrogen gas evolution. The presence of antimony at the negative plate surface also offers the possibility of toxic stibine gas (SbH_3) evolution under overcharge conditions. The mechanisms by which these processes occur have been pursued by various investigators[39-41].

A large number of minor elements naturally occur in commercial batteries, as a result of paste oxide manufacture, grid alloy corrosion, leaching from separators, and so on. Among the possible unfavorable effects of such impurities are capacity-loss, increased self-discharge (gassing), voltage lowering, and increased corrosion. The detrimental effects of cations such as Sb^{+3}, Fe^{+2}, Pt, Mn^{+4}, and Co^{+2}, and anions such as Cl^- and NO_3^- are well established[182-183].

Ferrous ions, Fe^{+2}, will be oxidized at the positive plate to the ferrous state, Fe^{+3}, then reduced at the negative to Fe^{+2}, resulting in both sets of plates running down on open circuit. Mn^{+4} and Co^{+2}, strong oxidizing agents, are known to have an adverse effect on organic separators. None of these elements, (Fe, Mn, Co) however, serves any useful purpose, although Co^{+2} is reported to increase the corrosion resistance of the positive grid, so they can be entirely avoided in grid alloy compositions. Chloride and nitrate ions in solution essentially constitute hydrochloric and nitric acid respectively. Both these acids will dissolve lead, so that grid corrosion is increased in their presence. Studies have been made of the effect of phosphoric acid additions to the electroltye, which is reported relieve the capacity-loss and grid passivation (sulfation) problems that occur particularly for Pb-Ca grids on float service[67].

25

One of the possible effects of impurities is modification of the crystal morphology of compounds formed during charging and discharging. While in theory, the reactions of the lead-acid battery are completely reversible, it must be realized that phase transformations between compounds must physically occur on each cycle. For example, during discharge of the positive plate, $PbSO_4$ crystals nucleate and grow at the expense of PbO_2 crystals, and the reverse occurs during recharge. In these transformations, the morphology of and contact between the respective reactants is of great importance; a gradual decrease in the effectiveness of the active material microstructure toward cyclic reactivity may be a major cause of the gradual loss of capacity observed during cycling. In this respect, changes in the nucleation and growth kinetics and crystal morphology of the reaction products, caused by the presence of foreign species, can obviously have a very important influence on the capacity-loss phenomena. The overall conductivity, cohesiveness, and porosity of the microstructure can be drastically affected in either a positive or negative sense, depending on the specific effect of a given impurity.

The acceleration of active material shedding from the positive plate by the presence of $BaSO_4$ in the positive paste has been studied. It has been shown that in the presence of $BaSO_4$, often used as a negative paste addition, finer crystals of $PbSO_4$ tend to form on the surface of the positive plate on discharge, and this tends to lead to increased shedding during cycling. $BaSO_4$ apparently provides more nucleating sites for $PbSO_4$ precipitation[162]. Carbon black added to positive plates is reported to increase porosity by encouraging the formation of finer particles in the active material[184].

Various commercial battery electrolyte additives, often purported in the past to cause battery rejuvenation, have been shown to be essentially useless elixers[185].

26

IV. SEPARATOR MATERIALS

In a storage battery, no positive plate may physically touch a negative plate, or else a short circuit will occur, and all the plates in that cell (element) of the battery will lose their stored energy. To prevent this, and yet be able to construct reasonably compact (energy-dense) batteries, thin inert sheets of non-conducting, yet porous, materials, called "separators," are inserted between plates. The separator is usually placed with the reinforcing ribs vertical and next to the positive plate, to provide greater electrolyte volume adjacent to the positive, where water formation during discharge causes dilution, and to minimize direct contact of the active material and separator material, which tends to have oxidizing effects on some separator materials. Glass fiber retainer mats are sometimes placed between the positive plate and separator to retard active material shedding and prevent separator oxidation. The reinforcing ribs of separators may be formed as an integral part of the separator profile by extrusion or pressing, or may be applied individually. These ribs are typically 0.015 to 0.020 inches in depth. Together with the base material diaphragm (web) thickness, typically about 0.020 inches; this gives a total separator thickness of about 0.035 to 0.040 inches.

The general requirements of separator materials are: (1) strength, (2) stiffness, (3) fine porosity, (4) electrical resistance, (5) chemical inertness, (6) thinness, (7) purity, (see Table 3). A great variety of materials and designs have been employed for this purpose in lead-acid batteries. In the original lead-acid cell constructed by Planté in 1859, sheets of flannel were used. Up until WWII, wood was used in commercial batteries, but was difficult to deal with, having to be carefully processed to remove organic substances which interferred with the cell electrochemistry. Therefore, more straightforward manufacturing processes were sought, using various "artificial" separator materials. Glass wool impregnated with latex or plastic resin, and sometimes mixed with a silaceous clay filler material, was one of the earliest composites developed.

Numerous materials based on microporous processing technology have been developed since WWII, including various types of rubber and plastics. These are usually formed by a "wet" process, wherein the plastic base is mixed with a plasticizer and a pore-forming filler material such as starch or salt. After fabrication of the separator profile by methods such as pressing or extrusion, the plasticizing agent is evaporated off and the pore-former is leached out, giving rise to the desired porosity. A less common "dry" processing method involves sintering of the base material, with or without filler. Sintered separators tend to have lower total porosity and larger pore diameter. Micro porous separators have also been developed in which oil or water droplets are utilized as the pore-forming agent. Many contemporary separator materials may also include a retained filler reinforcement material such as silica powder[186]. Currently, many separators are

27

also made based on fibrous materials such as paper pulp, usually impregnated with thermo-setting resin, which is cured by oven heating. Perhaps the most common SLI separator material at present is phenolic-impregnated cellulose[186].

The porosity of an effective separator material must be at least 50% total pore volume, and may be 80% or more in some cases. However, at the same time, a minimized individual pore diameter and uniform size are desirable to prevent penetration by active material crystals. Figure 19 is a SEM photomicrograph of the structure of a sintered PVC separator, showing the nature of the porous structure. Among the various contem-porary separator materials, microporous polyethylene has the smallest pores, with about 0.03 μm average pore diameter, as seen in Table 3. From the standpoint of chemical inert-ness, resistance to oxidation while in close proximity to the positive plates is most important; in this, polymeric separators are superior to paper pulp-based separators such as cellulose. Particularly for longer-lifetime batteries and higher-power batteries, it is likely that the use of polymeric materials will be more common[186].

Low electrical resistance is important in separator materials, particularly in higher power batteries. This can be aided by reduced thickness and and increased porosity. How-ever, a thinner separator will tend to be more prone to oxidation due to proximity with the positive plate. It is important to realize the difference between porosity (percentage open space by volume or area) and pore size (average pore diameter) in relation to elec-trical resistance. Current passage through the separator occurs by ionic diffusion in the electrolyte filling the pores; total current passed is proportional to porosity and independent of pore size. Most contemporary separators have a porosity of at least 60%, with an attainable thinness of 20 μm at most for the material.

Purity is of increasing importance in separators, dictated by the need for contamina-tion-free electrochemical operation, and in this respect, polymeric separator materials are superior to paper-pulp types[186]. Particularly for applications such as "maintenance-free" batteries, where hydrogen gas evolution due to water electrolysis must be minimized, impurities that may lower the hydrogen overvoltage, either while standing or during charge, must be avoided. There is another reason that paper pulp separators are generally consid-ered unsuitable for use in "maintenance-free" battery designs, which usually utilize Pb-Ca grid alloys; as has been discussed earlier, Pb-Ca grid alloys are more likely to encourage positive plate shedding and therefore shorting through or around the separator; for these reasons, a smaller pore diameter is desired and separator envelopes are preferred; the envelope separator design also requires that the separator material have the ability to be folded and sealed, which destinctly favors polymeric materials over cellulose-based materials.

28

V. CONNECTOR AND CONTAINER MATERIALS AND DESIGNS

Of less importance than some of the materials discussed earlier are the materials
which are employed for the electrical connectors and battery containers. However, even
in these categories, some interesting innovations have been introduced.

In order to form the negative and positive plate groups in each cell, the plate
lugs are welded together to a short strap/terminal. Then, to connect the cells of
the battery in series, the elements are placed in cell compartments such that the nega-
tive post of one cell is adjacent to the positive plate of the next. The adjacent cell
posts are then joined by an inter-cell connector of some sort, while the extreme outside
posts become the overall battery positive and negative terminals. All of these lugs,
straps, and terminals must be heavy enough to conduct the high currents of charging and
high-discharge rates without overheating. However, all of this material, typically pure
lead or a lead alloy, contributes weight, but is not participatory in the electrochemical
reactions of the cell, so that it is highly desirable to reduce the total weight of this
so-called "top lead." Many innovations in connector design and materials refer to reducing
this total weight. Another consideration is corrosion of these "top-lead" components,
which is completely undesirable. Acidic fumes and electrolyte contact within the con-
tainer are unavoidable, however, and even using the best exterior terminal seals, elec-
trolyte tends to "creep" out along the interfaces.

Traditionally, intercell (positive to negative) connections were made using short
straps joining each pair of cell posts, these connectors being located on the exterior
of the battery container cover joining to the protruding cell posts. Usually, joining
is by fusion welding, but in some cases bolted joints are used. More recently, it has
become common to utilize less bulky intercell connections made entirely within the con-
tainer, either through the intercell partitions or over the partitions. This greatly
reduces the total top-lead weight. Another basic innovation has been to utilize side-
located rather than top-located overall battery terminals, which is intended to reduce
weight and corrosion (due to removal from the environment near the top vents).

One of the major obstacles to mass-production of lead-acid batteries is associated
with the assembly and joining of the plate groups, elements, connectors, and terminals, to-
gether with the battery case, cover, vent plugs, and seals. A particular problem in this
regard is the requirement for rather careful fusion joining of components in the proximity
of other components which are vulnerable to thermal effects. Therefore, various assembly
innovations have been suggested.

Lighter weight and/or more conductive materials are sometimes used or have been
proposed, such as copper and aluminum alloys, sometimes heavily coated with lead. Reduc-
tions in weight and resistance are of particular importance for higher energy density and

higher power batteries. One of the major problems with the use of alternate metals as conductors relates to joining with lead components, and corrosion of the resultant joint when joining is accomplished. Some of the more innovative materials proposed for connectors include lead-coated/impregnated fiberglass mat.

Containers for contemporary automobile type batteries are usually a one-piece "monobloc" mold of plastic. The container material must be corrosion-resistant relative to the battery electrolyte, and must have sufficient mechanical toughness to withstand load, shock, vibration, and temperature extremes in service. Years ago these containers were made of heavily loaded thick-walled bituminous pitch. Subsequent usage of hard rubbers and plastics has allowed thinner, lighter containers to be fabricated. The container or "jar" is typically rectangular, with integral intercell partitions, and separate cover or covers (with terminal and vent openings) that must be joined to the container after assembly of the elements.

Generally speaking, containers for lead-acid batteries must have the following properties: (1) mechanical toughness (strength plus impact resistance), (2) chemical resistance to the electrolyte and environment, (3) lack of harmful poisoning effects on the electrolyte due to substances in the container, (4) creep resistance (for high operating temperatures), (5) flame retardation (fire-resistant), (6) easy molding and joining (of cover to box), (7) transparency. Items 2, 3, and 4 relate more to long-term deterioration modes which are more important in longer service batteries such as standby telephone batteries. Batteries with shorter lives, such as SLI types, which are repeatedly charged and discharged, are more typically limited by electrochemical performance failure of internal materials, particularly plate materials, so that long term effects are relatively insignificant. Item 7 (transparency) is also more important for long-life batteries, where inspection and service is facilitated by being able to see the interior of the battery. Glass "jars" have been widely used for this purpose in stationary applications. More recently, transparent plastics have been used. Associated with the introduction of injection-molded thin-walled polypropylene containers, the innovation involving through-the-partition intercell connectors was developed, which allowed reduction the so-called "top lead" weight contribution of connectors[187].

The plastic containers such as polypropylene also have the advantage that the container box and cover can be relatively simply and reliably jointed by heat-welding processes.

SUMMARY

Principles affecting the performance of materials in the lead-acid battery system have been reviewed here. In considering the various component materials, it is important to recognize their interrelationships. For many of these components, such as the separators and containers, the required properties have in effect been fully realized, in that further improvement in these materials would not greatly improve battery performance, if at all, and so efforts to further develop these materials are not extensive. Presently, the most critical materials are obviously those in the electrodes, particularly the active material/grid composite which makes up the positive plates. The character and integrity of this composite has been shown to have the most profound effect on the performance of contemporary lead-acid batteries. Recent application of advanced microanalytical techniques has been of great value in giving insight into the mechanisms of battery operation. These studies have shown that in particular the effects of cyclic electrochemical transformation between compounds in the active material mass are of great importance.

A distinction can be made between complete battery failure, characterized by unacceptable behavior such as inability to recharge, and less complete deterioration in performance, such as decreased capacity. The former type of failure is more easily diagnosed and characterized, while the latter is a more subtle deviation from optimum performance, and is more difficult to predict and explain. While it is not always clear exactly what the subtle microscopic mechanisms are which lead to capacity loss and active material disintegration in service, a number of viable possibilities have been explored. It is likely that a combination of the proposed mechanisms occurs in any case, and that different mechanisms dominate under different circumstances. For example, high discharge rates (high power service) yield different battery performance over the long-term than low-rate discharge conditions. Because of the long period of existence of the lead-acid battery system, battery technologists have long-established empirical procedures to handle many of the typical problems of various service routines. However, only recently have these service differences and responses begun to be clearly related to microscale features such as the transformation-induced character of the cycled active material mass. In a similar vein, it is important to recognize the wide variation in electrochemical history that can be experienced for a given battery type in service. Again, battery users have empirically developed approached to common problems. If and when the microscale effects of various service conditions is more completely known, it may be possible to better optimize the performance and extend the life of a given battery, such as by means of appropriate reparative routines. At present there is not a particularly useful connection established between macroscale operational variables in performance, and microscale interpretations of

mechanisms, in most battery systems. This is in contrast to the approximately parallel situation in corrosion engineering, where many practical problems have been successfully and routinely approached by means of laboratory-scale and even theoretical models. The future will certainly bring a closer connection between service problems and basic research into mechanisms of battery performance.

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LIST OF TABLES

42

Table 1a: Desired features of grid materials

Conductivity
Strength
Corrosion resistance
Passivation resistance
Electrochemical "cleanliness"
Compatibility with active material (adherence)
Fabricability (casting or working, joining)
Lightweight

Table 1b: Typical grid materials (all compositions with wt%)

Cast alloys

Pb-Sb based:

Pb-4.5 Sb-0.5 As-0.5 Sn-0.06 Cu (standard SLI batteries)
Pb-2.5 Sb-0.1 As   (+ small amounts Ag, Sn, Te, Se, S)("low maintenance batteries")

Pb-Ca based:

Pb-0.07 Ca-1Sn   ("maintenance free," submarine, and telephone batteries)

Pure lead

Wrought alloys

Pb-Ca-Sn: Pb-0.07 Ca-1Sn
D-S lead: Pb-4% PbO (by volume)
Pb-Cd-Sb: Pb-3Cd-2.5 Sb

Composite materials and designs

Lead-coated metals
Lead-coated plastics
Lead wire-plastic weave
Lead wire-carbon fiber weave

43

Table 2a: Desired features of active material

     Mechanical contiguity and stability
     Porosity
     Electrochemical activity
     Adherence to grid

Table 2b: Active material compounds

Pb	lead
PbO	litharge (yellow)(orthorhombic)
PbO	red PbO (tetragonal)
Pb_3O_4	red lead
$PbSO_4$	lead sulfate
$3PbO \cdot PbSO_4 \cdot H_2O$	tribasic lead sulfate
$4PbO \cdot PbSO_4$	tetrabasic lead sulfate
αPbO_2	lead dioxide (orthorhombic)
βPbO_2	lead dioxide (tetragonal)

Table 3a: Desired features of separator materials

> Strength
> Stiffness
> Porosity (maximum)
> Pore diameter (minimum)
> Electrical resistance
> Chemical inertness
> Thinness
> Purity
> Joinability

Table 3b: Typical separator materials for lead-acid batteries

Historical

Flannel

Wood (Port Orford Cedar, Douglas Fir)

Glass wool impregnated with latex or plastic resin

Contemporary	Volume Porosity, %	Minimum Pore Size, μ	Minimum Web Thickness (mils)
PVC (sintered)	48	25	13-14
PVC (microporous)	87	75	
Polyethylene (microporous)		0.03	10-18
Resin-bonded paper pulp	67	20	18
Latex-bonded diatomaceous earth	78	21	
Polyethylene/cellulose	70	33	
Nonwoven polypropylene		12	20
Rubber (microporous)	66	1.0	

Table 4a: Desired features of container materials

Mechanical toughness

Chemical resistance to electrolyte

Creep resistance

Flame retardation

Easy molding and joining

Transparency

Table 4b: Container materials for lead-acid batteries

Historical

Bituminous pitch

Glass-lined containers

Lead-lined containers

Hard rubber (clay-loaded)

Hard rubber (coal dust-loaded)

Resin rubbers

Contemporary

Resin rubbers

Plastics

Polystyrene

Polypropylene

Acrilonitrile - butadiene styrene copylymer (ABS)

Polyethylene

PVC

FIGURE CAPTIONS

Fig. 1   Primary lead phase dendrites (dark) and eutectic phase mixture network (light) in the as-cast microstructure of Pb-Sb alloys. Note the refinement effect of increased antimony concentration. (a) Pb-4 wt% Sb (b) Pb-8 wt% Sb. (Polarized light photomicrographs courtesy of VARTA Batterie AG).

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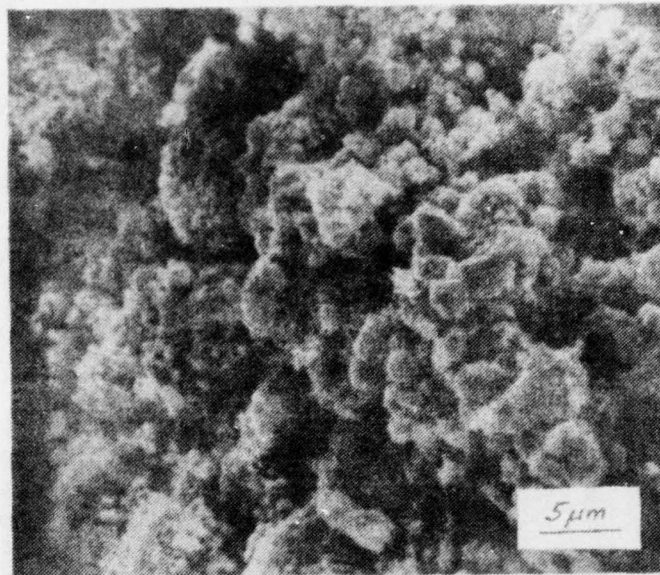
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47
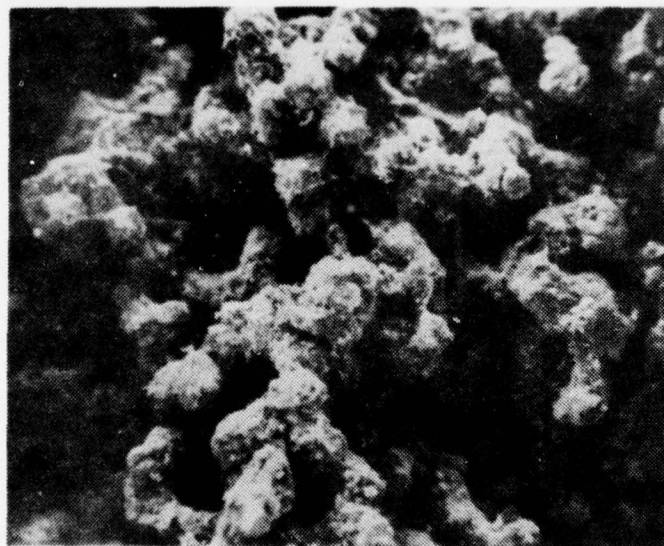
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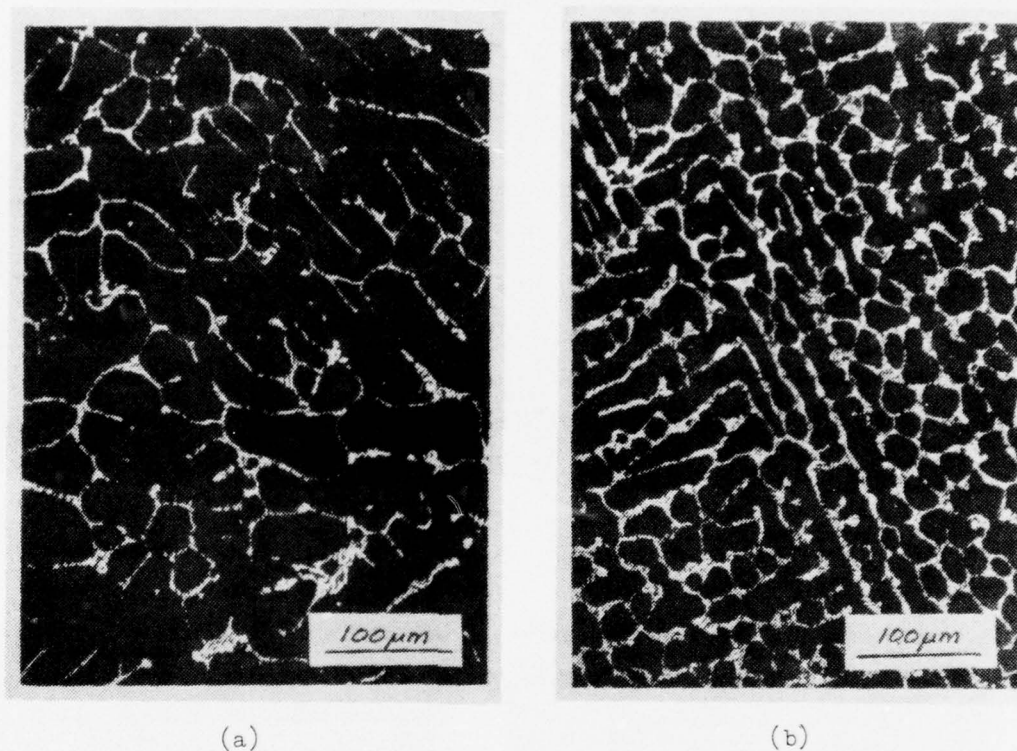
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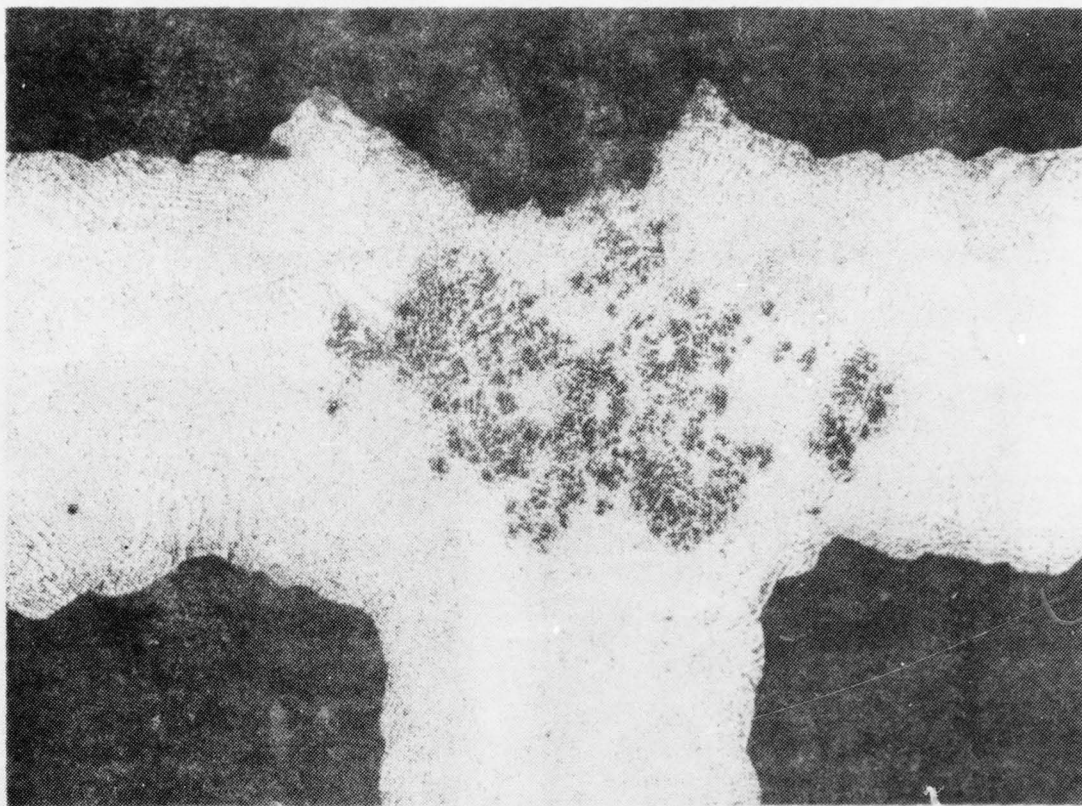
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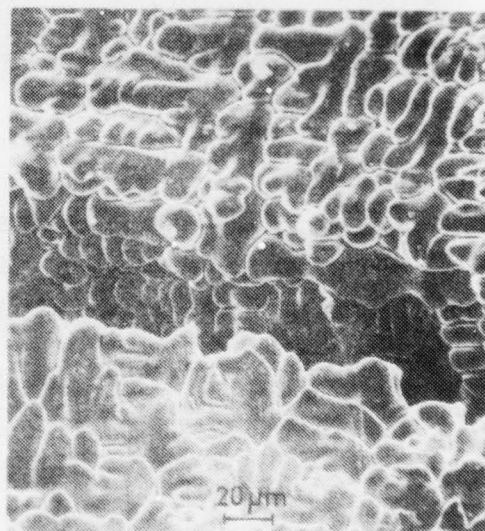

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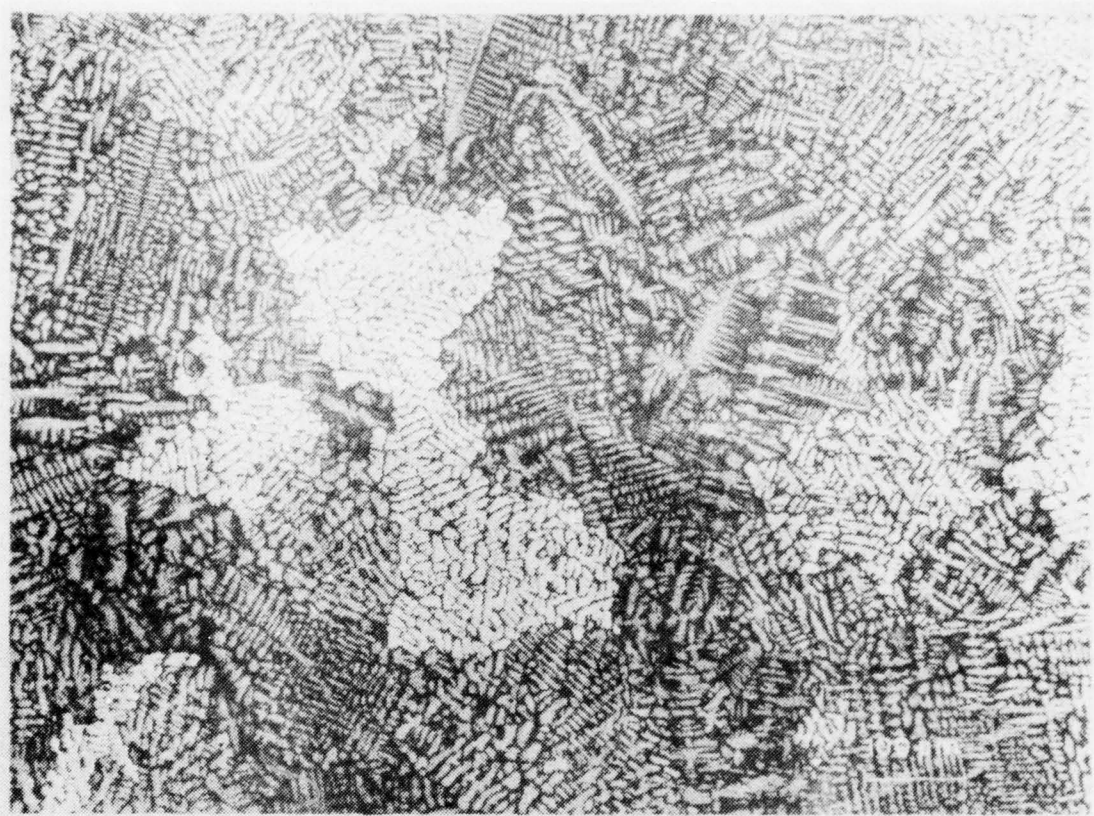
50

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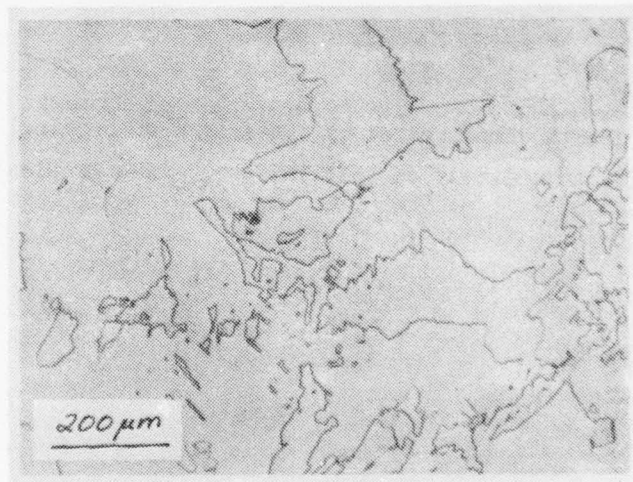lgesellschaft AG)

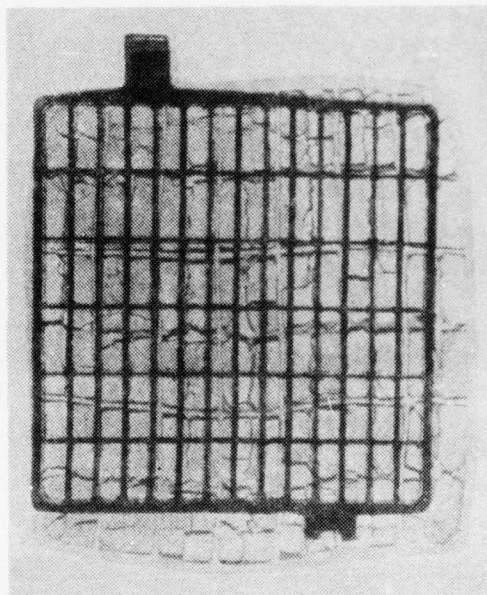Fig. 5   Microstructure of as-cast Pb-0.06 wt% Ca alloy.

51

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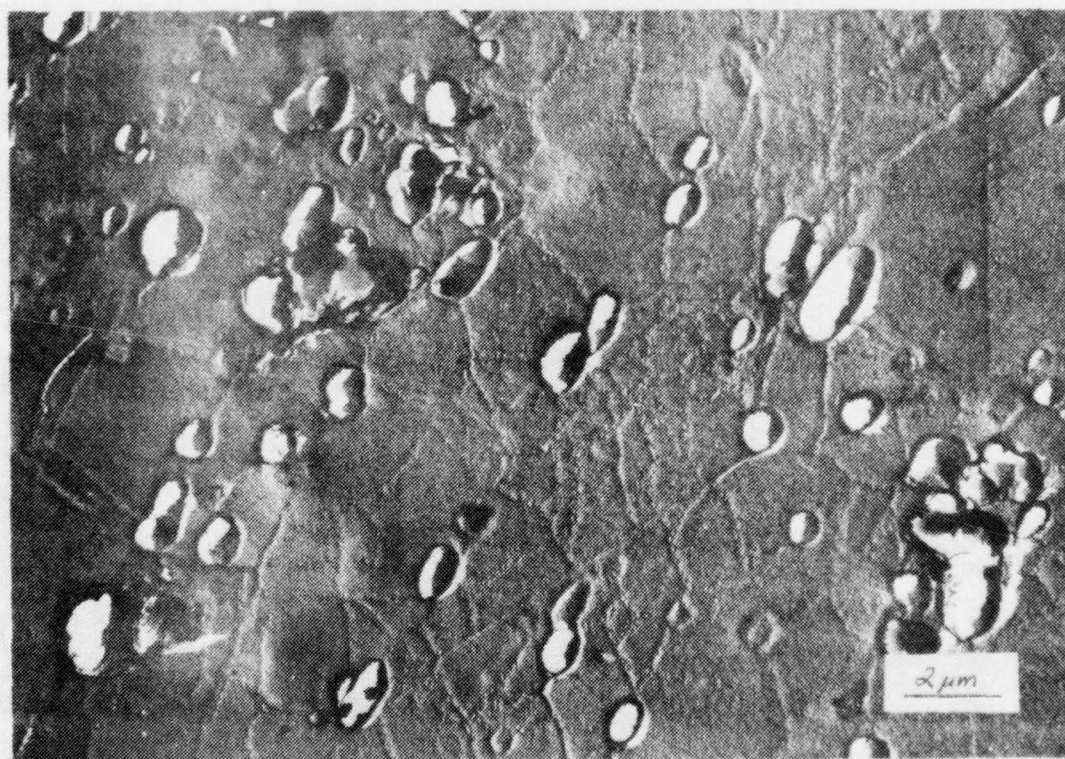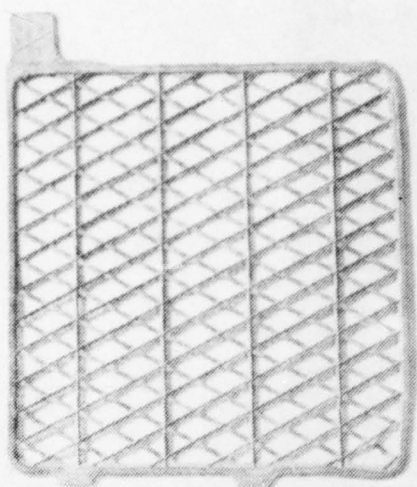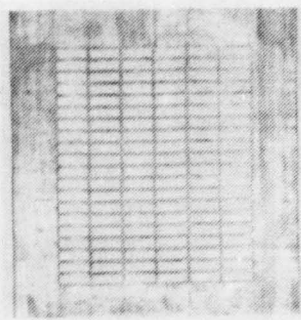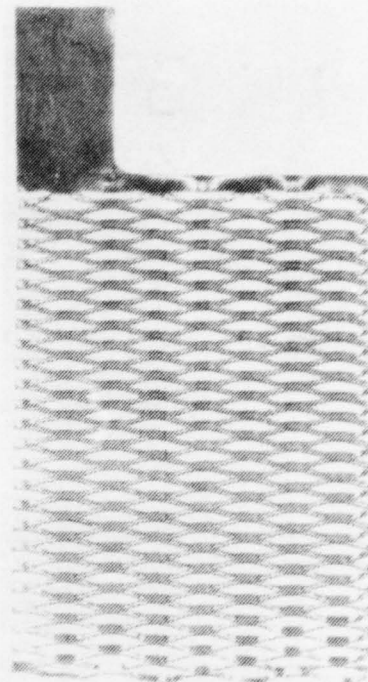

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53

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54

(g)

(h)

(i)

(j)

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55

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57

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59

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(b)

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60

10μm

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